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(71) Applicant (for all designated States except US): JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB).

(72) Inventors; and
(75) Inventors/Applicants (for US only): POLLINGTON, Stephen, David [GB/GB]; 17 Chancer Close, Emmer Green, Reading RG4 8PA (GB). POULSTON, Stephen [GB/GB]; 4 Hatherley Road, Reading RG1 5QA (GB). TORBATI, Reza [GB/GB]; 29 Merryman Drive, Crowthorne, Berks RG45 6TW (GB). RAJARAM, Raj Rao [MU/GB]; 34 Buckland Avenue, Slough SL3 7PII (GB).

(74) Agent: NUNN, Andrew, Dominic; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).

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(54) Title: EXHAUST SYSTEM INCLUDING HYDROCARBON SCR CATALYST

(57) Abstract: An exhaust system for an internal combustion engine comprises a first hydrocarbon selective catalytic reduction (HC-SCR) catalyst comprising a metal on a support, which support comprises alumina, titania, zirconia or, non-zeolite silica-alumina or a mixture or mixed oxide of any two or more thereof and a second, platinum-based HC-SCR catalyst disposed with and/or downstream of the first HC-SCR catalyst, wherein the exhaust system comprises means for coking the catalyst during normal engine operation.

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EXHAUST SYSTEM INCLUDING HYDROCARBON SCR CATALYST

This invention relates to an exhaust system for an internal combustion engine, and in particular it relates to an exhaust system including a hydrocarbon selective catalytic reduction catalyst comprising a supported metal.

In selective catalytic reduction (SCR) by hydrocarbons (HC), HC react with NOx, rather than with O_2, to form nitrogen, CO_2 and water according to equation (1):

$$\{HC\} + NOx \rightarrow N_2 + CO_2 + H_2O \tag{1}$$

The competitive, non-selective reaction with oxygen is given by Equation (2):

$$\{HC\} + O_2 \rightarrow CO_2 + H_2O \tag{2}$$

Two preferred groups of HC-SCR catalysts to selectively promote the desired reaction (1) for catalysing HC-SCR of NOx (HC-SCR catalysts are also referred to as "lean NOx catalysts" (LNC) or "DeNOx catalysts"). These are platinum on alumina and copper-substituted zeolite such as Cu/ZSM-5.

Pt-based catalysts tend to operate at relatively low temperature (peak activity ~250°C) and have a relatively narrow temperature window for HC-SCR activity. Another problem is that the popular Pt/Al_2O_3 favours the formation of N_2O over N_2 at relatively low temperatures.

Zeolite-based HC-SCR catalysts have a wider temperature window than Pt-based HC-SCR catalysts and also operate at higher temperatures (peak activity ~400°C). However, a problem associated with zeolite-based HC-SCR catalysts such as Cu/ZSM-5 is that they can become deactivated in use through lean hydrothermal ageing. This is caused by sintering of the copper component and/or de-alumination of the zeolite.

One approach to address the problem of limited temperature window is to combine two or more HC-SCR catalysts (e.g. to combine both Cu/ZSM5 and Pt-based catalysts together) to extend the operating window of the catalysts (see e.g. K.C. Kharas et al. SAE 982603). Another approach is to include a HC trap component in the exhaust

5   system upstream or on the HC-SCR catalyst that adsorbs HC when the exhaust gas is at a temperature below the light-off temperature of the catalyst, and desorbs the HC when the catalyst is at or above light-off temperature (see for example EP-A-0830201). However, neither approach addresses the problem of zeolite-based HC-SCR catalyst deactivation.

10   Research into alternative and improved HC-SCR catalysts continues to be published in the literature. In "Surface properties and reactivity of Cu/γ-Al$_2$O$_3$ catalysts for NO reduction by C$_3$H$_6$ Influences of calcination temperatures and additives", T.-W. Kim et al., App. Cat. A: Gen. 210 (2001), 35, the authors refer to prior reported studies which show that certain supported metal oxide catalysts, such as alumina supported

15   copper and copper aluminate, have similar HC-SCR activities compared with Cu/ZSM-5. The Kim et al. paper describes investigations into how calcination temperatures affect the activity of the copper-based catalysts.

Others have investigated Cu/ZrO$_2$ (K.A. Bethke et al., Catalysis Today 26

20   (1995), 169 and C. Montreuil et al. in US-A-5,155,077) and Cu-Zr mixed oxide systems (K.A. Bethke et al. Catalysis Letters 25 (1994), 37) for NOx reduction with hydrocarbon. However, G.P. Ansell et al., (205th ACS National Meeting, Denver, 29th March-1 April 1993) report that the activity of Cu/ZrO$_2$-type materials is severely inhibited by the presence of water in the gas feed, a component often omitted in the reported tests

25   involving these catalysts.

F. Figueras et al., Catalysis Today 42 (1998), 117 have reported that Cu on sulfated zirconias leads to an increase in NOx reduction activity for HC-SCR using decane as the hydrocarbon when compared with the un-sulfated support. Pasel et al.,

30   Applied Catalysis B 25 (2000), 105 have studied a number of metal supported sulfated ZrO$_2$ systems including Cu using propane as the reductant.

US patent No. 6,202,407 describes a system in which HC is injected in a pulsed manner upstream of a HC-SCR catalyst e.g. Cu on Al_2O_3. The document explains that NO_x conversion in the system does not drop to zero when HC injection is stopped.

5   We have now devised an exhaust system comprising at least two specific HC-SCR catalysts, which system having a broader overall temperature window of NO_x reduction activity.

According to a first aspect, the invention provides an exhaust system for an
10   internal combustion engine, which exhaust system including a first hydrocarbon selective catalytic reduction (HC-SCR) catalyst comprising a metal on a support, which support comprises alumina, titania, zirconia or, non-zeolite silica-alumina or a mixture or mixed oxide of any two or more thereof, and a second, platinum-based HC-SCR catalyst disposed with and/or downstream of the first HC-SCR catalyst, wherein the exhaust
15   system comprises means for coking the catalyst during normal engine operation.

An advantage of the invention is that the temperature at which the first HC-SCR catalyst stores activated HC is also within the temperature range at which the second, Pt-based catalyst is effective for HC-SCR. The activation of the first catalyst at this
20   temperature only results in a HC conversion of ~10% over the first catalyst. Hence up to 90% of the HC is available to the Pt-based catalyst for HC-SCR disposed with and/or downstream thereof. The activated first HC-SCR catalyst is available for HC-SCR at higher temperatures. Furthermore, the Pt-based catalyst can oxidise the CO produced by the preferred HC-SCR catalyst according to the invention as a by-product of generating
25   the activated hydrocarbon species.

By "coking" we mean contacting the catalyst with elevated quantities of hydrocarbon. We believe that this procedure leads to the formation of adsorbed activated hydrocarbon (or "coke") species on the catalyst surface.

30

By "elevated" herein, we mean that the quantities of hydrocarbon to which the catalyst is exposed are in excess of those quantities that would contact the catalyst during normal engine operation.

4

The coking means can be used to form the coke species on the catalyst surface by any convenient process e.g. by contacting a suitable HC liquid onto the catalyst surface, but preferably it is by introducing hydrocarbon into the exhaust gas. Preferred means for introducing hydrocarbon include at least one of: means for injecting the hydrocarbon into the exhaust gas; means for adjusting the ignition timing of at least one engine cylinder; and means for adjusting the engine air-to-fuel ratio.

Advantageously, the hydrocarbon is the fuel that powers the engine. The engine can be a stationary engine, but where it is used to propel a vehicle, this avoids the need to carry more than one source of hydrocarbon.

At its most fundamental, the means for coking the catalyst can expose the catalyst continuously to elevated amounts of hydrocarbon. However, we prefer that the exposure to hydrocarbon is intermittent and that the coking means further comprises means for controlling the coking process. Preferably, the control means includes a pre-programmed electronic control unit (ECU). For example, the ECU can carry "maps" to expose the catalyst to hydrocarbon responsive to driving conditions e.g. use of accelerator, engine revs and/or responsive to feedback from on-board diagnostics such as exhaust gas or catalyst temperature sensors, tailpipe NOx sensors etc.

Preferably, the catalyst is exposed to hydrocarbon responsive to the catalyst temperature which can be measured directly or estimated according to exhaust gas temperature. For example, the control means can coke the catalyst at between catalyst temperatures at which hydrocarbon oxidation commences over the catalyst and peak NOx conversion occurs. For catalysts for use in the present invention, this can occur in the temperature range 200-450°C, preferably 250°C to 350°C. Selective addition of HC at specific catalyst temperatures leads to improved utilisation of the added HC and so greater fuel economy.

A feature of the invention is that the HC-SCR catalyst are chosen to have improved resistance to hydrothermal ageing compared with zeolite-based HC-SCR catalysts. The metal in the HC-SCR catalysts can be present in the form of an oxide, but as the skilled person will appreciate, in use the oxide may react with exhaust gas

components to form a hydroxide, a carbonate, a sulfate or a nitrate, for example. All compound forms of the metal are embraced by the present invention.

The supported metal can be a transition metal such as V, Cu, Cr, Ni, Mn, Fe, Ga or Co or mixtures of any two or more thereof. Presently, copper is the preferred transition metal. Catalysts can become sulfated in use through contact with sulfur species in the exhaust gas derived from HC fuel or HC lubricant. Most preferably the catalysts are pre-sulfated, i.e. by sulfating the catalyst prior to inserting it into an exhaust system.

Without wishing to be bound by theory, we believe that supports capable of forming particularly stable sulfates are more useful in the present invention because they have increased acidity compared with the non-sulfated support. The support can comprise alumina, titania, zirconia, non-zeolite silica-alumina or a mixture or mixed oxide of any two or more thereof. In particular the alumina can be of any particular type, such as α, θ, δ or γ. However, presently, the γ form is preferred. The support can be stabilised (or doped) with Si, W, Mo, Nb or P. Dopants are typically present in the form of oxides but in use may be in the form of sulfates, nitrates, hydroxides etc.

A preferred HC-SCR catalyst according to the invention is at least one of alumina supported copper and zirconia supported copper. A mixture of CuO, Al_2O_3 and $CuAl_2O_4$ is particularly preferred.

The transition metal loading of the support material can be chosen as appropriate, but we have found that loadings of from between 5 and 20 wt.% based on the support are adequate.

The preferred catalysts for use in the present invention are advantageous as they have lower selectivity to N_2O formation than Pt-based catalysts and generally are active at higher temperatures than Pt-based catalysts. Lean hydrothermal ageing and lean hydrothermal sulfur ageing (LHSA) of Cu-zeolite catalysts at 550°C for prolonged periods of e.g. 16 hours or more leads to severe deactivation. However, we have found that LHSA of 10 wt.% Cu/Al_2O_3 and 10 wt.% Cu/sulfated zirconia actually improves HC-SCR activity.

We believe that the increase in activity obtained by the sulfur promotion, i.e. the sulfation of the catalyst, arises due to increased HC activation by acidic sulfur sites and formation of coke species that are active for HC-SCR. The activation step in which the catalyst is pre-treated with hydrocarbon leads to increased activity as it effectively leads to storage of activated hydrocarbon species on the catalyst.

One interesting application of the preferred catalysts according to the invention is that it may not be necessary to continuously inject additional HC into the exhaust system upstream of the HC-SCR catalyst in order to improve the efficiency of NOx reduction over the HC-SCR catalyst (so-called "Active DeNOx"). Injection of hydrocarbon at 200-300°C in diesel applications followed by a temperature ramp in a gas mix not containing HC still results in good NOx conversion. This process can effectively improve fuel economy by allowing more efficient use of the hydrocarbon for NOx reduction.

This observation has application in treating HC emissions at lower exhaust gas temperatures, e.g. immediately after cold-start, wherein the catalyst is formulated in a composition including an adsorber, such as a zeolite e.g. ZSM-5, ß-zeolite or mordenite, as explained in our EP-B-830201. The adsorber can adsorb HC at relatively low temperatures, below the temperature at which the HC-SCR catalyst is active for reducing NOx, and desorb the HC at a relatively higher temperature when the catalyst is active. By matching the temperature window of adsorption/desorption of the adsorber with the temperature window of activity of the catalyst it is possible to improve HC treatment in the exhaust system.

In a further aspect, the HC-SCR catalysts and catalyst compositions according to the invention can be used in the exhaust treatment system of an internal combustion engine, preferably a diesel engine and most preferably a heavy-duty diesel engine (as defined by the relevant European or US Federal or California State legislation). However, the engine can be powered by alternative fuel means such as CNG, LPG or methanol, and engines powered by these alternative fuels are within the scope of the present invention.

The preferred catalysts according to the invention can be made by methods known in the literature. For example, as described in G. Delahay *et al.*, Journal of

Catalysis 175 (1998) 7, the Figueras *et al.* paper above or J. Pasel *et al.* App. Cat. B: Environ. 25 (2000) 105. These include sulfation using sulfuric acid, impregnation using a sulfate-containing metal pre-cursor e.g. $CuSO_4$ (aq), or by lean hydrothermal sulfur ageing.

As the skilled person will be aware, hydrocarbon fuels such as diesel fuels include sulfur-containing species. As a result, the exhaust gases produced by its combustion can include sulfur-containing species such as SOx, e.g. SO_2 and SO_3, or organic species which can be adsorbed to volatile organic fraction or soluble organic fractions of the particulate matter. Thus, catalysts inserted in the exhaust system of an engine will be exposed to sulfur-containing species and may be sulfated as a result. Accordingly, one process for making the catalysts according to the present invention is to insert an unsulfated catalyst in the exhaust system of an engine and allowing it to become sulfated. However, pre-sulfation of the catalyst is presently preferred because control of the sulfation process can be controlled.

According to a further aspect, the invention provides a method of reducing NOx with a hydrocarbon in an exhaust gas of an internal combustion engine using a first hydrocarbon selective catalytic reduction (HC-SCR) catalyst including a metal on a support which support comprises alumina, titania, zirconia or, non-zeolite silica-alumina or a mixture or mixed oxide of any two or more thereof and a second, platinum-based HC-SCR catalyst disposed with and/or downstream of the first HC-SCR catalyst, which process comprising intermittently coking the first catalyst at a catalyst temperature between that at which oxidation of hydrocarbon commences on the first catalyst and peak NOx conversion occurs by contacting the first catalyst with a hydrocarbon and contacting the coked first catalyst with the exhaust gas at a temperature where NOx reduction occurs, and converting NO_x in the exhaust gas over the second HC-SCR catalyst with hydrocarbon which slips the first HC-SCR catalyst.

In order that an aspect of the invention may be more fully understood, reference will now be made to the following Examples by way of illustration only and with reference to the accompanying drawings, in which:

Figure 1 is a graph showing the adsorption of n-$C_{10}H_{22}$ (400 ppmC$_3$) in full gas mixture without NOx at 250°C and 300°C on a sulfated 10%Cu/Al$_2$O$_3$ catalyst;

Figure 2 is a graph showing NOx reaction with the pre-adsorbed n-$C_{10}H_{22}$ of

5   Figure 1;

Figure 3 is a graph showing the NOx and CO conversions of a Cu/sulfated zirconia catalyst formed by CuSO$_4$ impregnation onto ZrO$_2$;

10   Figure 4 is a graph showing the NOx and CO conversions of a Cu/ZrO$_2$ catalyst formed by Cu(NO$_3$)$_2$ impregnation onto ZrO$_2$;

Figure 5 is a graph showing the effect of pre-"coking" the catalyst of Figure 3 on NOx and CO conversions;

15

Figure 6 is a graph showing the effect of pre-"coking" the catalyst of Figure 1 on NOx conversions; and

Figure 7 is a graph comparing the NH$_3$ TPD for the catalyst of Figures 3 and 4

20   and a sulfated ZrO$_2$ control.

EXAMPLE 1

Cu/Al$_2$O$_3$ powder catalyst preparation

25

Catalyst preparation followed known methods in the literature, such as those described by Delahay, Figueras and Pasel mentioned above. More specifically, the 10wt%Cu/Al$_2$O$_3$ catalyst (based on the total weight of the support) was prepared by wet impregnation using a copper nitrate (aq) copper precursor. The catalyst was dried and

30   calcined in air at 500°C for 2 hours and then at 800°C for a further 2 hours. XRD analysis suggests that this process produces a product including a mixture of CuO, Al$_2$O$_3$ and CuAl$_2$O$_4$. Sulfation was by lean hydrothermal ageing in air, SO$_2$ (50 ppm) and 5% H$_2$O at 550°C.

EXAMPLE 2

HC-SCR NOx activity of Cu/Al$_2$O$_3$ powder catalyst

The activity of the powder copper catalysts of Example 1 were measured at a
mass hourly swept volume (MHSV) of 200 litres per hour per gram (0.6 gram and
2 litres per minute) in a simulated exhaust gas mixture of 200ppm NOx, 400ppmC$_3$
(propene equivalent [measured by FID/THC analyser]) n-C$_{10}$H$_{22}$, 14% O$_2$, 5.1% CO$_2$,
750ppm CO and 20ppm SO$_2$. The gas mixture was adjusted to remove at least one of the
HC and NOx as appropriate.

Figure 1 shows HC consumption over the catalyst at 250°C or 300°C in the
absence of NOx. The HC was then removed from the gas mixture and the catalyst was
allowed to cool to 200°C. NOx was then added to the gas mixture and the temperature
was ramped up at 10°C per minute to 550°C. As a control, an identical sample was also
exposed at 250°C without NOx or HC present. In another test, after HC exposure at
250°C, the sample was ramped up in NO$_2$. The NOx conversion using the pre-adsorbed
HC is shown in Figure 2.

As can be seen, in the absence of any adsorbed HC, the NOx conversion was
negligible, whilst pre-adsorbing the HC gives significant NOx conversion with the
highest conversion activity achieved with the NO$_2$.

EXAMPLE 3

Preparation of Cu/ZrO$_2$ and Cu/Al$_2$O$_3$ pelletised powder catalyst

A sulfated 10wt%Cu/ZrO$_2$ was prepared following known methods in the
literature by impregnation of ZrO$_2$ with CuSO$_4$, drying and calcining the powder in air at
500°C. This support is referred to as "SZ" or sulfated zirconia. For comparison, a non-
sulfated 10wt%Cu/ZrO$_2$ catalyst was prepared by impregnating of ZrO$_2$ with Cu(NO$_3$)$_2$
(aq) and calcining in the same way. A 10wt%Cu/Al$_2$O$_3$ powder catalyst was prepared
similarly to Example 1, except that no 800°C calcination step was performed and the
sulfation was done with sulfuric acid. The powder catalysts were pelletised and particle
sizes in the range of 250<d<355 μm were used for subsequent experimentation.

EXAMPLE 4

HC-SCR NOx activity of Cu/ZrO$_2$ pelletised powder catalyst

The activity measurements have been performed with n-$C_{10}H_{22}$ or propene as the

5   HC species. The following conditions were used: NO 200ppm, CO 745ppm, CO_2 5.1%,

O_2 14%, H_2O 4.6%, 400ppmC_3 (propene equivalent [measured by FID/THC analyser]),

SO_2 20ppm, N_2 balance at a MHSV of 200 L h^{-1} g^{-1}. Unless otherwise indicated the data

were collected in ramp up mode, 10°C/min, from 150°C.

10   Figure 3 shows the NOx and CO conversions of the Cu/SZ catalyst of Example 3.

With repeat runs the NOx conversion and CO production both increased. Figure 4 shows

the Cu/ZrO$_2$ system made with a nitrate precursor of Example 4. The NOx conversion is

lower, though still increases slightly with repeat ramps, and there is no sign of CO

production.

15

Conclusions

Since we have shown previously that a sulfated Cu/ZrO$_2$ catalyst prepared by

impregnation of $Cu(NO_3)_2$ on sulfated ZrO_2 are strongly inhibited by water (see

20   G.P. Ansell paper above), these results suggest a competition between water and a

hydrocarbon-derived component for active sites on the catalyst. The formation of this

hydrocarbon-derived component would appear to be promoted by the increased acidic

nature of the catalyst.

25   Peak NOx conversion appears to be related to the ability of the catalyst to

produce CO indicating that the hydrocarbon is being only partially oxidised in the

temperature window for NOx conversion. We have also observed that the NOx

conversion of these materials increases with repeated use.

30

EXAMPLE 5

In order to show that the improvement in NOx conversion with repeat use of the

systems described in Example 4 is linked to the formation of coke species on the catalyst

surface, we performed tests to probe the effect of catalyst pre-treatment on subsequent NOx conversion activity. In these tests the catalyst is held at constant temperature for a period of time in the gas mix described in Example 4, then quickly cooled it to 150°C before increasing the temperature ramp-wise at 10°C/min.

5

Figure 5 shows the effect of this 'coking' procedure on the 10wt%Cu/SZ. Both CO production and NOx conversion increase with the length of time the catalyst is "pre-treated" by exposing it to the full gas mix at 250°C. An explanation for this effect is that the pre-treatment effectively leads to storage of activated hydrocarbon species on the catalyst surface which are subsequently used for NOx reduction. At the pre-treatment temperature, ~15% of the hydrocarbon is converted. In all these experiments the temperature ramp is started at 150°C at which temperature there is no hydrocarbon conversion and no effect of pre-treatment. This should avoid coking occurring before the temperature ramp begins. Figure 6 shows similar data for the pelletised sulfated Cu/Al_2O_3 catalyst according to Example 3. The CO production again increases with NOx conversion for this catalyst.

EXAMPLE 6

20   In order to investigate the mechanism for improved NOx conversion over a coked catalyst for use in the present invention, we tested a H_2SO_4 impregnated ZrO_2 catalyst using the synthetic gas mixture described in Example 4, also including 200ppm NO_2. Even after coking at 250°C this sample gave NOx conversions significantly less than 10%. We believe, therefore, that the NOx conversion mechanism for sulfated Cu/support catalysts may require some synergy between the Cu and the support. Figure 7 shows the NH_3 temperature-programmed desorption (TPD) profiles for the Cu/SZ ($CuSO_4$ precursor) and Cu/ZrO_2 ($Cu(NO_3)_2$ precursor) of Example 3 and a sulfated ZrO_2 control. The profile shows that the Cu/ZrO_2 ($Cu(NO_3)_2$ precursor) has similar acidity to the sulfated ZrO2 sample but the NOx conversion over the Cu-containing catalyst is higher. The Cu/SZ ($CuSO_4$ precursor) sample has much higher acidity.

CLAIMS:

1.   An exhaust system for an internal combustion engine, which exhaust system including a first hydrocarbon selective catalytic reduction (HC-SCR) catalyst comprising a metal on a support, which support comprises alumina, titania, zirconia or, non-zeolite silica-alumina or a mixture or mixed oxide of any two or more thereof, and a second, platinum-based HC-SCR catalyst disposed with and/or downstream of the first HC-SCR catalyst, wherein the exhaust system comprises means for coking the catalyst during normal engine operation.

2.   An exhaust system according to claim 1, wherein the coking means includes means for introducing a hydrocarbon into an exhaust gas.

3.   An exhaust system according to claim 2, wherein the hydrocarbon introducing means comprises at least one of: means for injecting the hydrocarbon into the exhaust gas; means for adjusting the ignition timing of at least one engine cylinder; and means for adjusting the engine air-to-fuel ratio.

4.   An exhaust system according to any preceding claim, wherein the hydrocarbon is the fuel that powers the engine.

5.   An exhaust system according to any preceding claim, wherein the coking means further comprises means for controlling the coking process, preferably in order that coking is intermittent.

6.   An exhaust system according to claim 5, wherein the control means cokes the catalyst between temperatures at which hydrocarbon oxidation commences over the catalyst and peak NOx conversion occurs.

7.   An exhaust system according to claim 6, wherein the control means cokes the catalyst at between 200-450°C, preferably 250-350°C.

8.   An exhaust system according to claim 5, 6 or 7, wherein the control means includes a pre-programmed electronic control unit.

9.   An exhaust system according to any preceding claim, wherein the first HC-SCR catalyst supported metal is a transition metal.

5   10.   An exhaust system according to claim 9, wherein the transition metal is V, Cu, Cr, Ni, Mn, Fe, Ga or Co or mixtures of any two or more thereof.

11.   An exhaust system according to any preceding claim, wherein the first HC-SCR metal catalyst component is a metal oxide.

10

12.   An exhaust system according to any preceding claim, wherein the support for the first HC-SCR catalyst is stabilised with Si, W, Mo, Nb or P.

13.   An exhaust system according to claim 12, the first HC-SCR catalyst comprises

15   alumina supported copper or zirconia supported copper.

14.   An exhaust system according to claim 13, wherein the first HC-SCR catalyst comprises a mixture of CuO, Al_2O_3 and $CuAl_2O_4$.

20   15.   An exhaust system according to any preceding claim, wherein the metal loading in the catalyst is 5-20 wt.% based on the support.

16.   An exhaust system according to any preceding claim, wherein the first HC-SCR catalyst is sulfated.

25

17.   An exhaust system according to any preceding claim, wherein the second platinum-based HC-SCR catalyst is Pt/Al_2O_3.

18.   An exhaust system according to any preceding claim, further comprising a HC

30   adsorber, preferably upstream of the supported metal catalyst according to claim 1.

19.   An exhaust system according to claim 18, wherein the HC adsorber comprises a zeolite.
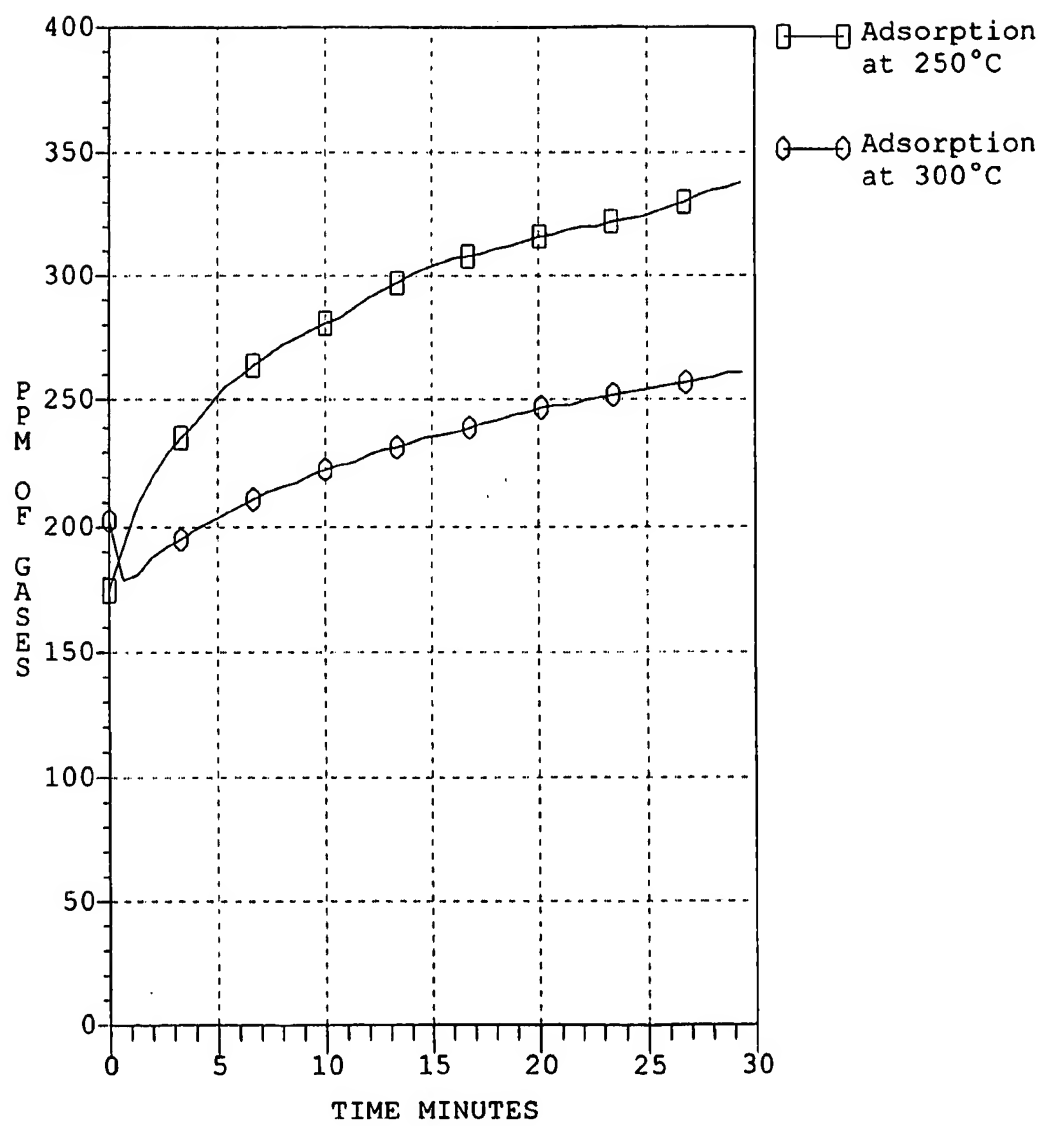
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20.   An internal combustion engine including an exhaust treatment system according to any preceding claim.

21.   An engine according to claim 20, wherein it is a diesel engine, preferably a heavy-duty diesel engine.

22.   A method of reducing NOx with a hydrocarbon in an exhaust gas of an internal combustion engine using a first hydrocarbon selective catalytic reduction (HC-SCR) catalyst including a metal on a support which support comprises alumina, titania, zirconia or, non-zeolite silica-alumina or a mixture or mixed oxide of any two or more thereof and a second, platinum-based HC-SCR catalyst disposed with and/or downstream of the first HC-SCR catalyst, which process comprising intermittently coking the first catalyst at a catalyst temperature between that at which oxidation of hydrocarbon commences on the first catalyst and peak NOx conversion occurs by contacting the first catalyst with a hydrocarbon and contacting the coked first catalyst with the exhaust gas at a temperature where NOx reduction occurs, and converting NO_x in the exhaust gas over the second HC-SCR catalyst with hydrocarbon which slips the first HC-SCR catalyst.
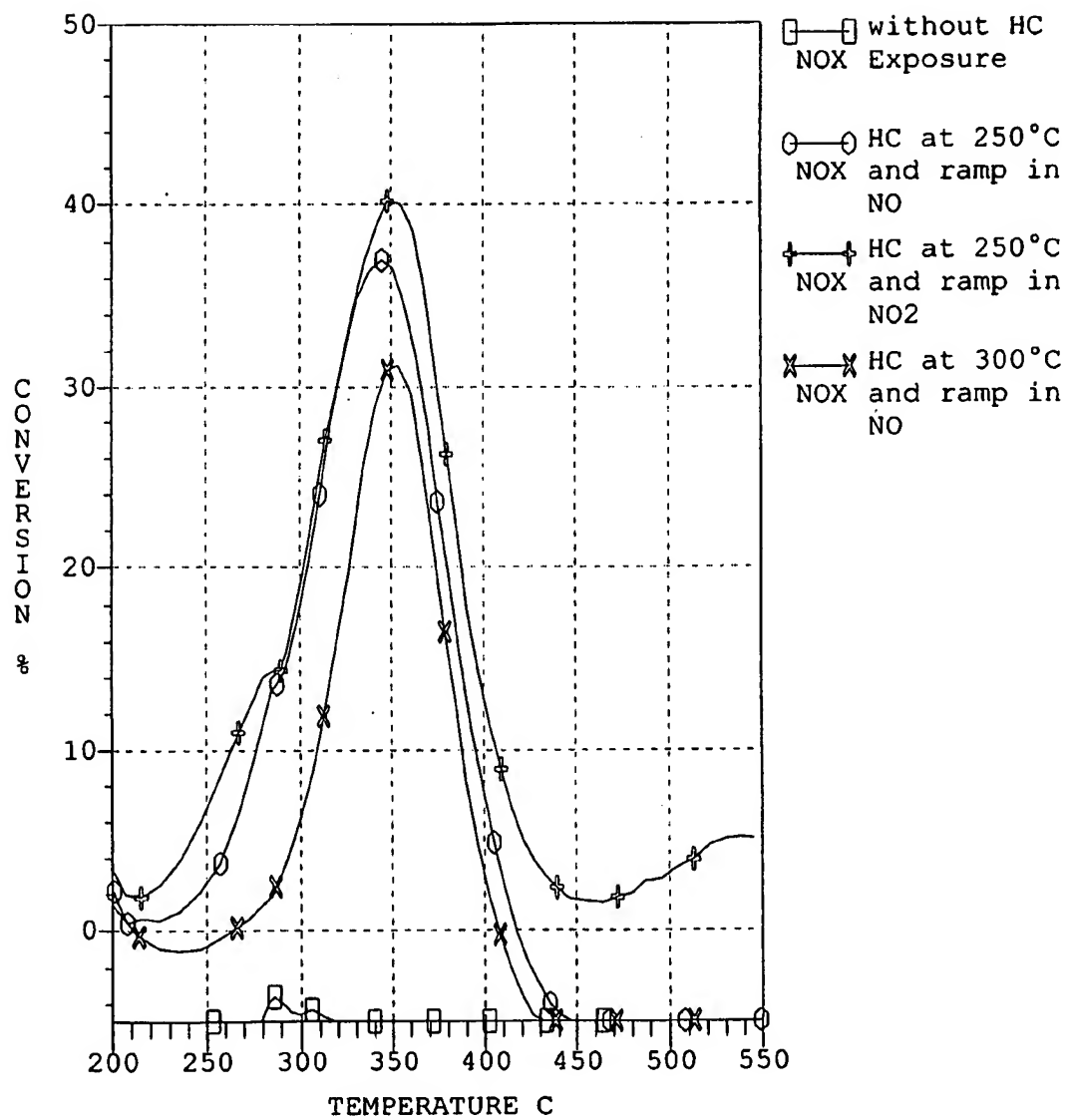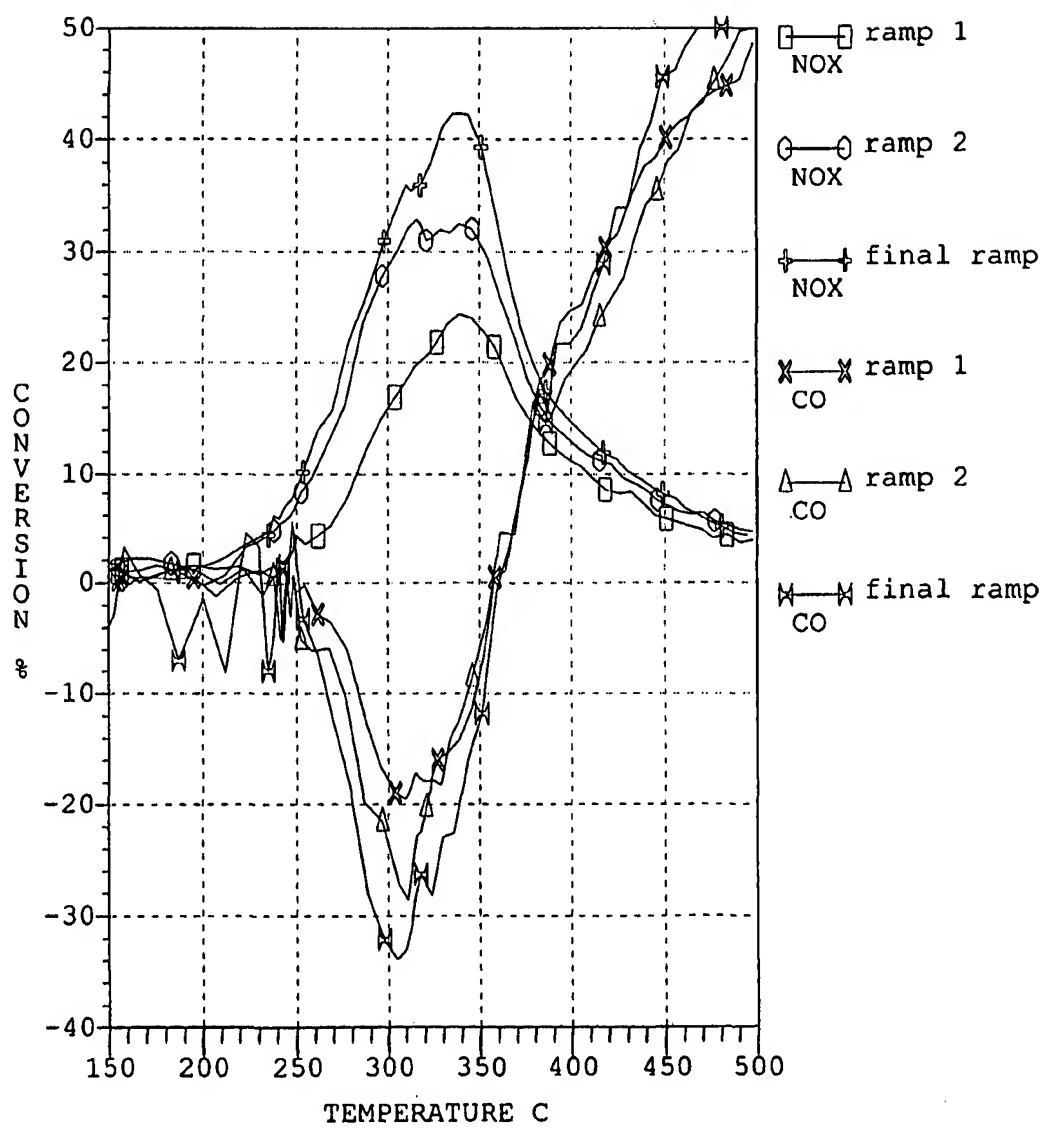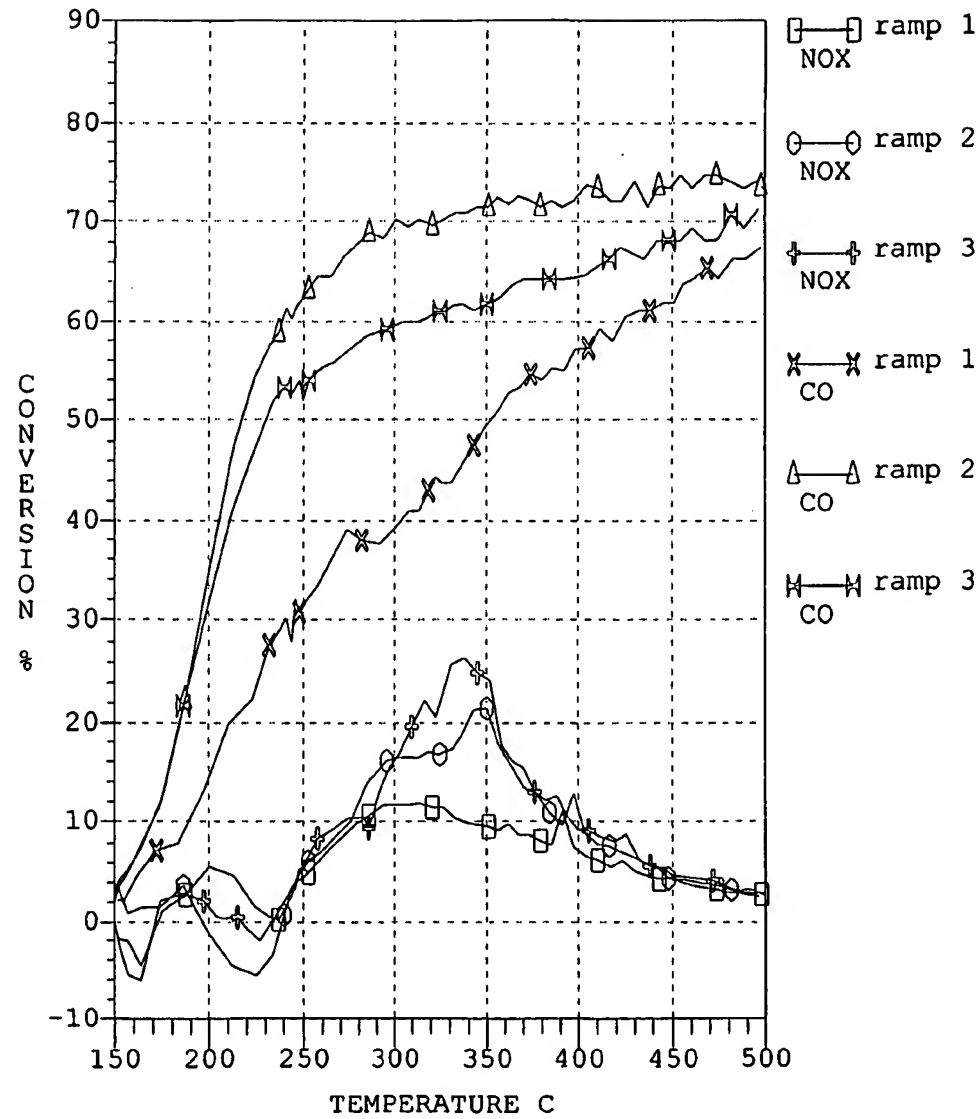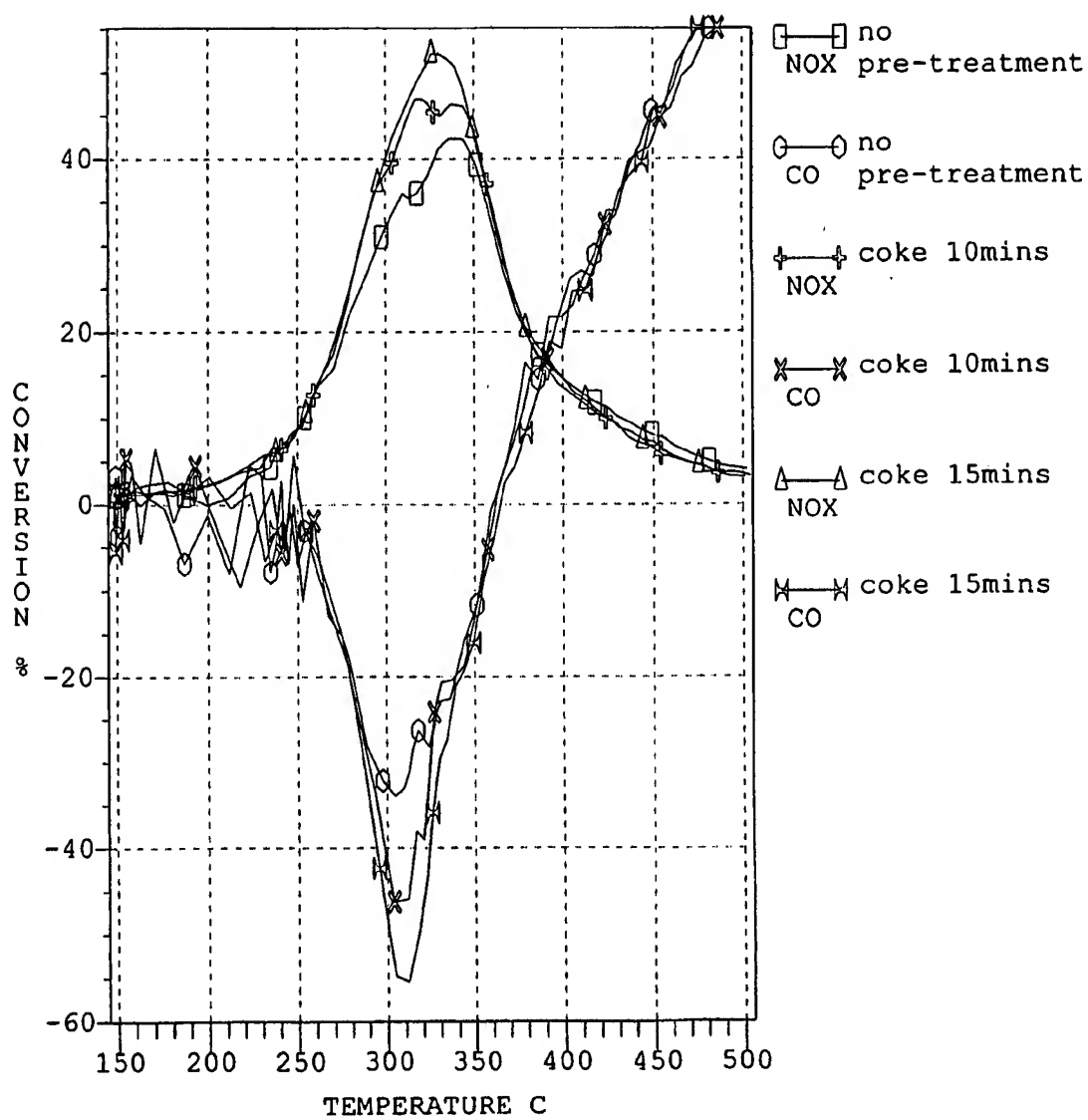
Figure 1

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Figure 2

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Figure 3

Figure 4
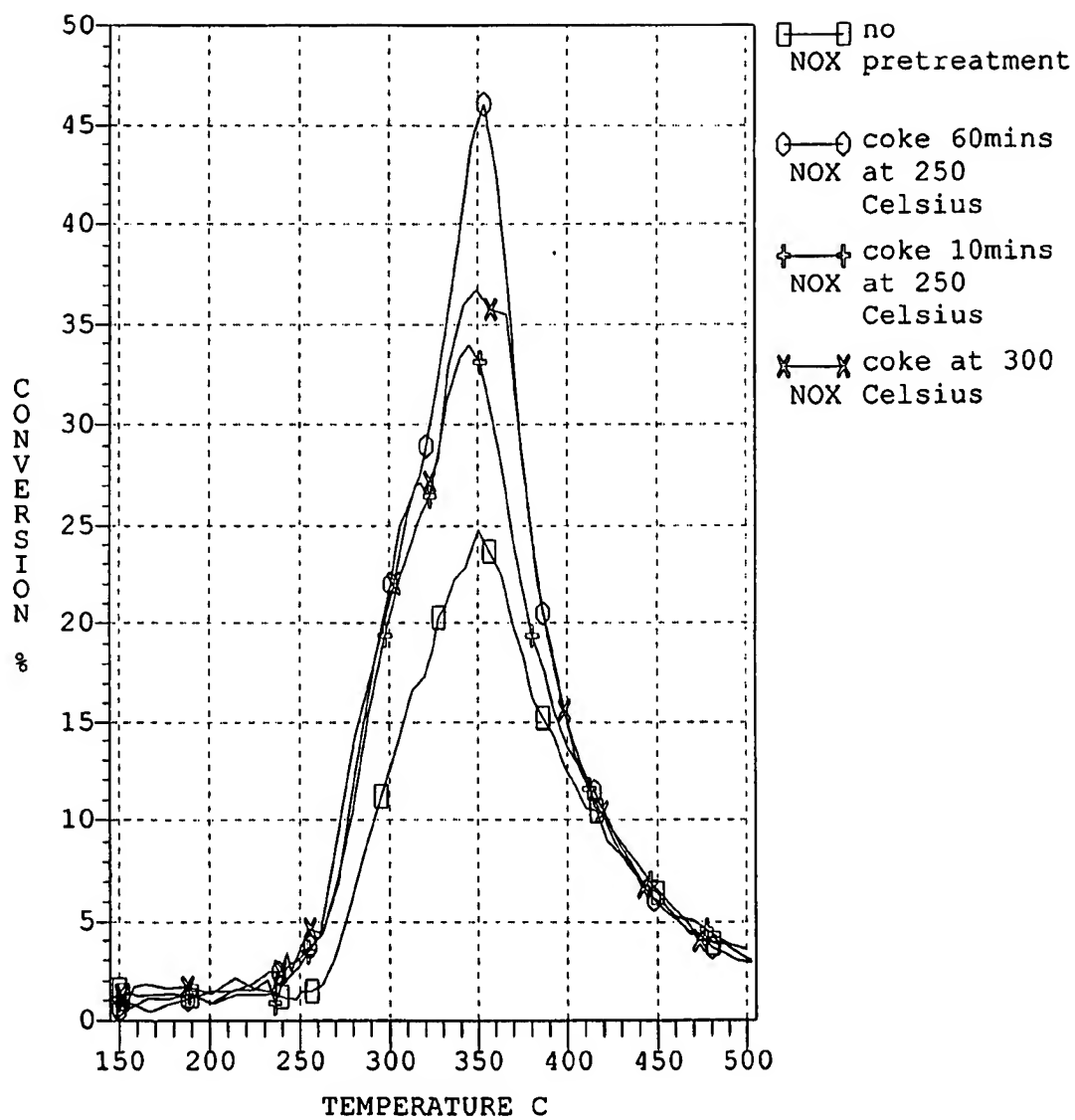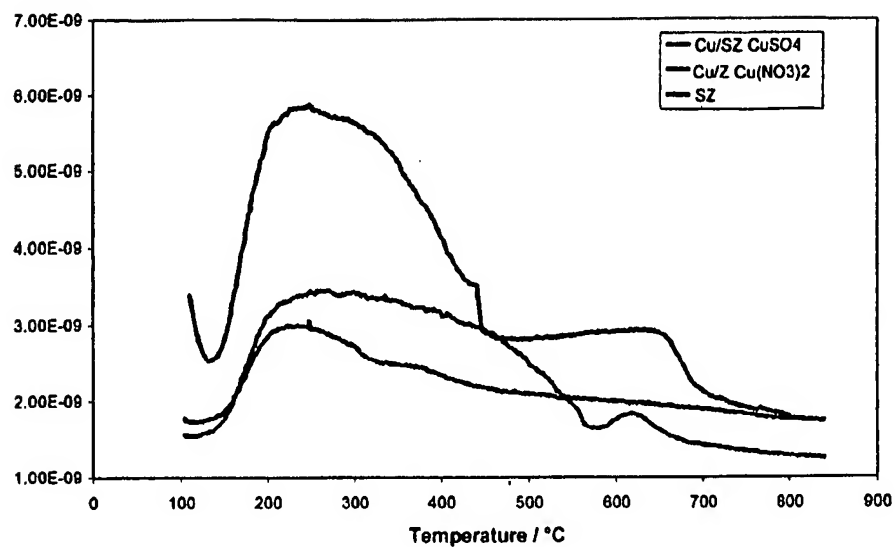
Figure 5

Figure 6

Figure 7

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/94

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 947 235 A (MAZDA MOTOR) 6 October 1999 (1999-10-06) column 2, line 12 -column 3, line 9 column 12, paragraph 50 column 14, paragraph 57 column 16, line 1 - line 7 column 19, line 46 - line 55; claims 1-15; figure 1 ---	1-4, 9-15,17, 20-22
X	GB 1 458 514 A (TOYODA CHUO KENKYUSHO KK) 15 December 1976 (1976-12-15) page 2, line 56 -page 3, line 94 --- -/--	1-4, 9-15, 20-22

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

'A' document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
15 January 2003	22/01/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Eijkenboom, A

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